ORGANIC CHEMISTRY

Short Answer Questions:

1. Explain the following with suitable examples?

a) Wurtz Reaction.

b) Kolbe's Electrolysis.

c) Friedal Craft's Alkylation

Ans. a) Wurtz Reaction: Alkyl halides on treatment with sodium metal in dry ethereal solution give higher alkanes. This reaction is known as Wurtz reaction and is a convenient method for the preparation of higher alkanes having even number of carbon atoms. Usually bromides and iodides are preferred.

$$\mathbf{R–X + 2Na + X–R \xrightarrow[ether]{Dry} R–R + 2NaX}$$

E.g. Methyl bromide on treating with sodium metal in dry ether gives ethane.

$$CH_3Br + 2Na + CH_3Br \xrightarrow{Dryether} CH_3 - CH_3 + 2NaBr$$

b) Kolbe's Electrolysis:

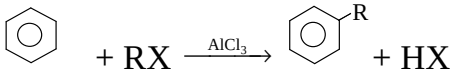
When a saturated aqueous solution of sodium or potasium salt of a carboxylic acid is electrolysed, alkane containing even number of carbon atoms along with carbondioxide at anode and sodium or potassium hydroxide along with hydrogen are formed at cathode.

$$2RCOONa + 2H_2O \longrightarrow R–R + 2CO_2 + 2NaOH + H_2$$

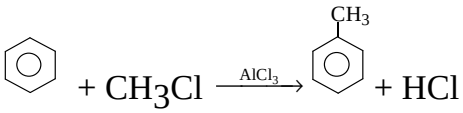
E.g. When a concentrated aqueous solution of sodium acetate is electrolysed, ethane is liberated at anode.

$$\mathbf{2CH_3COONa + 2H_2O \longrightarrow CH_3–CH_3 + 2CO_2 + 2NaOH + H_2}$$

c) Friedal Craft's Alkylation: Benzene reacts with an alkyl halide in presence of anhydrous aluminium chloride to give alkyl benzene.



E.g. Benzene reacts with methyl chloride in presence of anhydrous aluminium chloride to give methyl benzene i.e. Toluene.

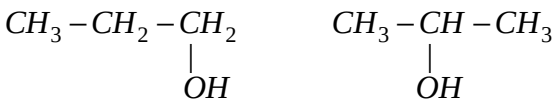


2. Explain position isomerism and Functional group isomerism with examples?

Ans. Position Isomerism:

Isomers which differ in the position of a functional group or multiple bond or substituent in the same carbon chain are called position isomers.

Eg1: C_3H_7OH has two position isomers.



n-Propyl alcohol (1-propanol) Isopropyl alcohol (2-propanol)

Eg2: Butene has two position isomers.

$CH_3CH_2CH=CH_2$ $CH_3CH=CHCH_3$

1-Butene 2-Butene

Functional Group Isomerism:

Compounds having same molecular formula but different functional groups are called functional group isomers.

Eg1. CH_3CH_2OH and $CH_3–O–CH_3$

Ethyl alcohol Dimethylether

Eg.2 CH_3CH_2CHO **and** CH_3COCH_3

Propionaldehyde Acetone

Eg.3 CH_3CH_2COOH **and** CH_3COOCH_3

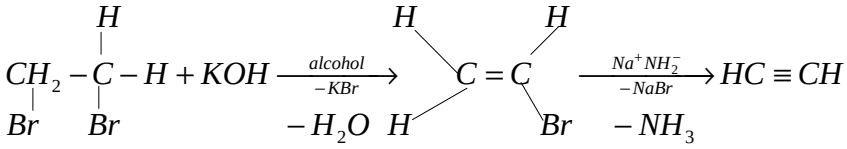
Propionic acid Methyl acetate

3. **Give two methods of preparation of Acetylene. How does it react with water and Ozone?**

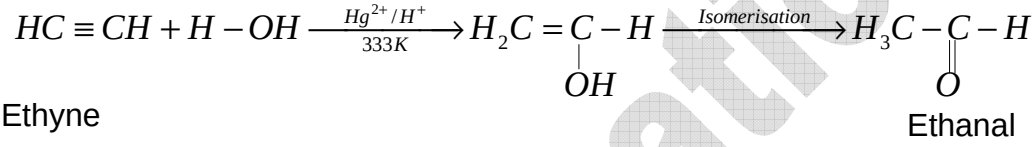
Ans. **From Calcium Carbide:** On industrial scale, Ethyne is prepared by treating Calcium Carbide with water

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

From vicinal diHalides: Vicinal dihalides on treatment with alcoholic potassium hydroxide undergo dyHydroHalogenation. One molecule of Hydrogen Halide is eliminated to form Alkenyl halide which on treatment with Sodamide gives Alkyne.



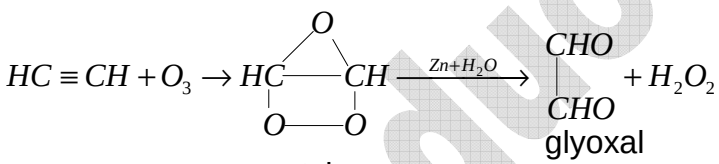
i. **Reaction with water:** One molecular of water adds to Ethyne on warming with mercuric sulphate and dilute Sulphuric acid at 333K to form Ethanal.



Ethyne

Ethanal

ii. **With ozone:** Ethyne undergoes reductive Ozonolysis to form glyoxal



acetylene ozonide

glyoxal

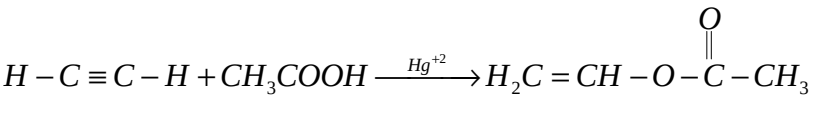
4. **How does Acetylene react with the following reagents? Give the corresponding equation and name the products formed in the reactions.**

a) Acetic acid **b) Water** **c) Hydrogen**

d) Halogens **e) Hydrogen Halide** **f) Ammonical** $AgNO_3$ **and** Cu_2Cl_2

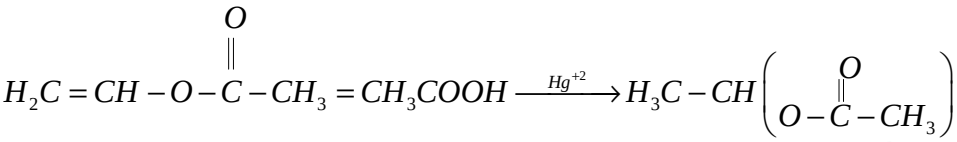
A) Acetylene being unsaturated molecule readily undergoes addition reactions with the π-bonds.

i) Reaction with Acetic Acid: - Acetylene on treatment with acetic acid gives vinylacetate in the 1st step and then gives Ethylidene diacetate Hg^{+2} acts as a catalyst.



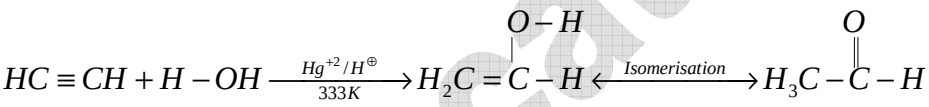
(Used in plastic industry)

Acetylene Vinyl acetate

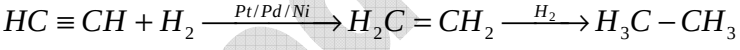


Vinyl acetate Ethylidene diacetate

ii) Reaction with water:- Acetylene undergoes addition reaction with water molecule warming with Mercuric sulphate and dilute Sulphuric acid at 333K to form Acetaldehyde (Ethanal)

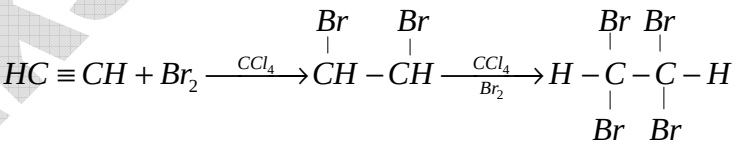


iii) With Hydrogen: Hydrogen molecule reacts with Acetylene in the presence of Pt/Pd/Ni to form ethane.



Ethyne Ethene Ethane

iv). With Halogens: on reaction with Bromine (Halogen) Acetylene forms a Tetrabromo product



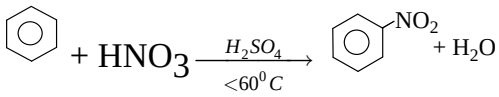
1,2-didromo ethane 1,1,2,2 –Tetra bromo ethane

In this reaction reddish Orange colour of Bromide gets decolourised. This reaction is used as a test for unsaturation.

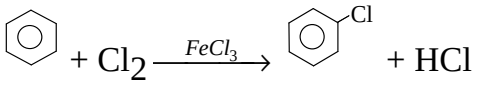
5. What is substitution reaction? Explain any two substitution reaction of benzene?

Ans. The reaction in which an atom or a group attached to a carbon atom in a substrate molecule is replaced by another atom or group is known as a Substitution reaction.

Nitration: Benzene when heated with a mixture of (1: 1 by volume) concentrated nitric acid and concentrated sulphuric acid **(nitration mixture)** below 60^0 C gives nitrobenzene.



Halogenation: Benzene reacts with chlorine or bromine in presence of Lewis acids such as $FeCl_3$ or $FeBr_3$ or $AlCl_3$ as catalyst to give halobenzene.



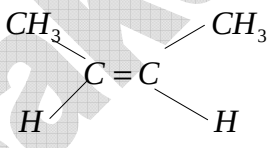
6. **What do you understand about Geometrical isomerism? Explain the Geometrical isomers of 2-butene.**

Ans. Geometrical isomerism: - Compound which possess the same molecular formula and same structural formula but differ in the spatial arrangement of the groups around the double bond are called Geometrical isomers and the phenomenon is known a Geometrical isomerism. This isomerism is also called cis-Trans isomerism

(a) Cis-Trans: Geometrical isomerism requires the two groups attached to the same carbon to be different

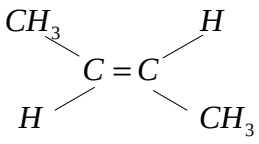
Alkenes of the type $abC=Cab$, $abC=Ccd$, $abC=Cax$ and $abC=Cbx$ show Geometrical isomerism. When the same groups lie on the same side of double bond then isomer is cis-isomer. If the similar groups are present on opposite side of double bond then it is Trans-isomer.

E.g.: - 2 butane



Cis-2-Butane

(Same groups are on same side)



Trans -2-Butane

(Same group are on opposite side)

7. Explain the method of writing E-Z configuration for geometrical isomers taking $CHCl = CFBr$ as your example.

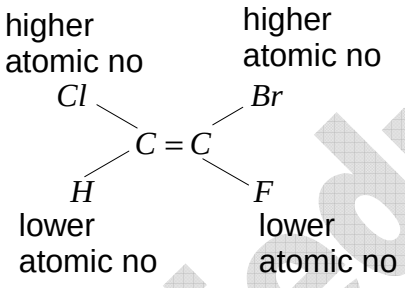
Ans. E-Z configurations:

i) E-Z notational system is used when it is not clear, which substituent on one carbon is similar to a reference substitute on the other. This is based on atomic number ranking method.

ii)According to this when atoms of higher atomic number are on the same side of double bond it is said to have 'Z' configuration. 'Z' stands for the German word 'Zusammen' which means together.

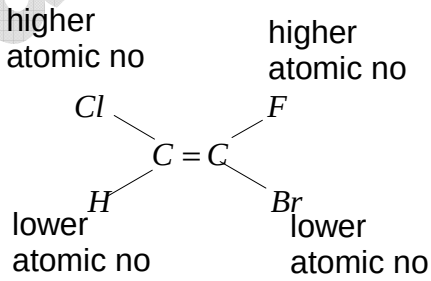
iii) When atoms of higher atomic number are on opposite sides of the double bond it is said to have 'E' configuration. 'E' stands for the German word 'Entgegen' which means opposite.

E.g.: $CHCl = CFBr$



Z-configuration

(Two higher priority groups $_{17}Cl$ and $_{35}Br$ same side)



E-configuration

(Two higher priority groups $_{17}Cl$ and $_{35}Br$ are on opposite side)

8. Write any two methods of preparation of Benzene? How does Benzene react with the following reagents?

a) CH_3Cl / anhydrous$AlCl_3$ b) $O_3/Zn+H_2O$

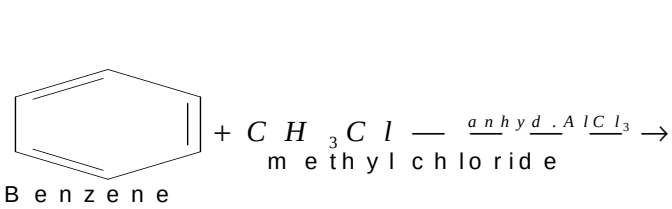
Ans. Polymerisation of acetylene: On passing acetylene gas through red hot iron or copper tube benzene is formed.

$$3C_2H_2 \xrightarrow{red\ hot\ tube} C_6H_6$$

Decarboxylation of Benzoic Acid: On heating sodium benzoate with soda lime gives benzene. It is a laboratory method of preparation.

$$C_6H_5COONa + NaOH \xrightarrow{CaO} C_6H_6 + Na_2CO_3$$

a.



b. **Ozonolysis:** One mole of benzene reacts with three moles of ozone to give a triozonide, which on hydrolysis in presence of zinc gives three moles of glyoxal.

$$C_6H_6 + 3O_3 \longrightarrow C_6H_6O_9 \xrightarrow{H_2O,\ Zn} 3\begin{matrix}CHO\\|\\CHO\end{matrix} + 3H_2O_2$$

9. Describe any two methods of preparation of Ethylene. Give equations for the reaction of ethylene with the following

a) Ozone **b) Hypohalous acid**

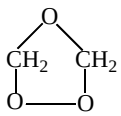
c) Cold and alkaline $KMnO_4$ **d) Heated with O_2 at high pressures**

Ans. Ethylene is prepared by the dehydration of ethylalcohol using Conc.H_2SO_4 at 170° C or Al_2O_3 at 350° C.

$$CH_3CH_2OH \longrightarrow CH_2 = CH_2 + H_2O$$

Ethylene is prepared by the dehydrohalogenation of ethylchloride using alcoholic NaOH or KOH.

$$\mathbf{CH_3CH_2Cl + KOH\ (alcoholic) \longrightarrow CH_2 = CH_2 + KCl + H_2O}$$

a. $CH_2{=}CH_2 + O_3 \longrightarrow$  $\xrightarrow[H_2O]{Zn}$ 2HCHO(Formaldehyde)

b. With Hypochlorous acid

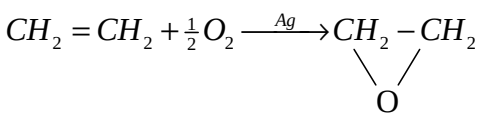
$$CH_2 = CH_2 + Cl{-}OH \longrightarrow CH_2Cl{-}CH_2OH \text{ (2-chloro ethanol)}$$

c. Baeyer's reagent oxidises ethylene to ethylene glycol.

$$CH_2 = CH_2 + H_2O + (O) \longrightarrow HO–CH_2–CH_2–OH$$

Ethane–1,2-diol

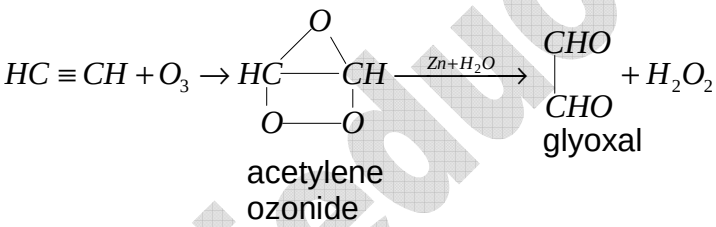
d. Ethylene is oxidised to ethylene oxide with air or oxygen in presence of silver catalyst.



10. What is ozonolysis? Which type of compounds reacts with ozone? Explain with anexample?

Ans. Unsaturated hydrocarbons undergo addition with ozone to form unstable ozonides which when hydrolysed in presence of zinc, carbonyl compounds are formed. The overall reaction is called ozonolysis or reductive ozonolysis. Unsaturated hydrocarbons having C=C or C≡C only undergo ozonolysis.Ozonolysis reaction is highly useful in detecting (or locating) the position of the double bond in alkenes or triple bond in alkynes.

E.g.

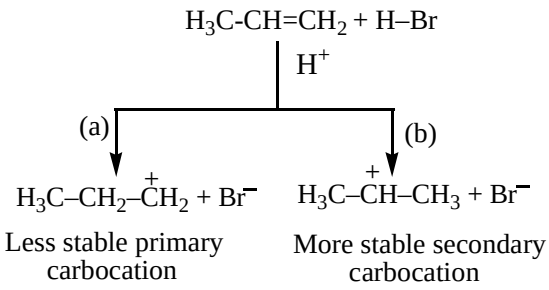


11. Discuss Markownikoff's Rule and kharash effect?

Ans. Markovnikov rule: This rule is useful when a polar reagent adds on to an unsymmetrical alkene. It states that "The negative part of the addendum adds on to the carbon atom having less number of hydrogen atoms".

Mechanism of the addition of hydrogen bromide to an unsymmetrical alkene is given as follows:

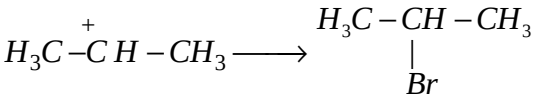
HBr ionises as H^+ and Br^-. Electrophile, H^+ attacks the double bond to form carbocation.



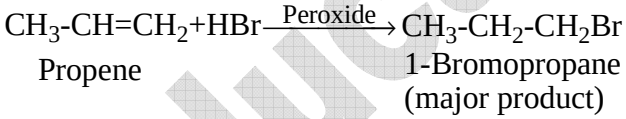
Due to more hyperconjugation in secondary carbocation (b), it is more stable than primary carbocation (a) and forms predominently at a faster rate. Then the secondary carbocation

(b) isattacked by Br^- readily to form the major product

2-bromopropane.



Peroxide Effect: In the presence of peroxide, addition of HBr to unsymmetrical alkenes takes place contrary to Markovnikov's rule. This happens only with HBr but not with HCl and HI. This reaction is also known as Kharasch effect or Anti Markovnikov's rule.

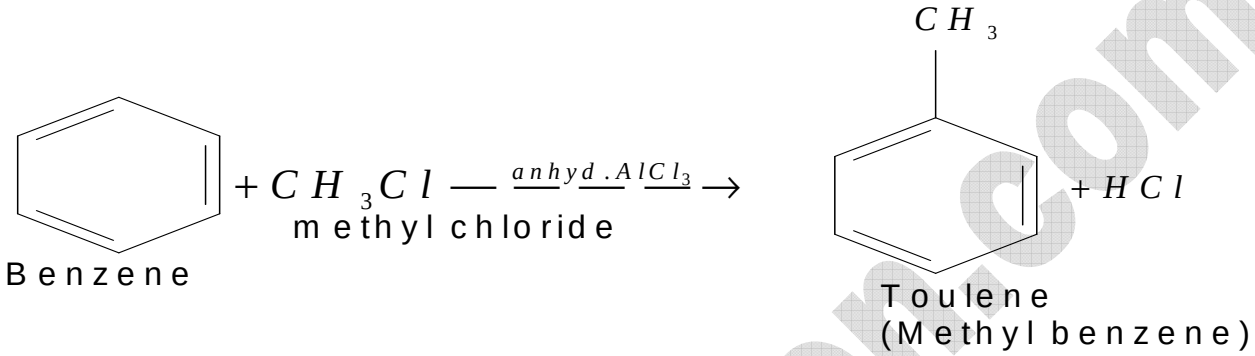


It follows free radical mechanism

Very Short Answer Questions

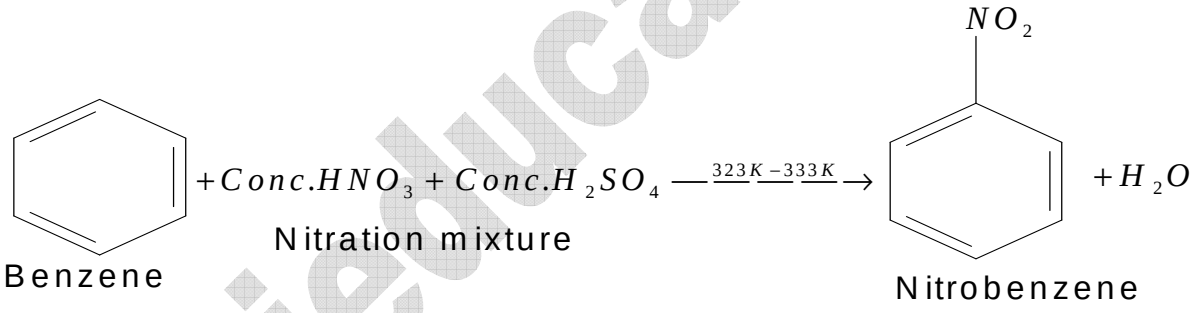
1. **Write the reagents required for the conversion of Benzene to Methyl Benzene?**

Ans. Benzene on reaction with methyl chloride in the presence of Anhydrous $AlCl_3$ gives Methyl Benzene. It is an Electrophic Substitution reaction.



2. **How is Nitro Benzene Prepared?**

Ans. When Benzene is heated with a mixture concentrated Nitric acid and concentrated Sulphuric acid (Nitration mixture) gives Nitro Benzene.



3. Write the corresponding equations for the following reactions and name the products A, B, and C?

$$CaC_2 \xrightarrow{H_2O} (A) \xrightarrow{redhottube} (B) \xrightarrow{AlCl_3+CH_3Cl} (C)$$

Ans. $CaC_2 + 2H_2O \xrightarrow{-Ca(OH)_2} C_2H_2(A) \xrightarrow{redhottube} C_6H_6(B) \xrightarrow{AlCl_3+CH_3Cl} C_6H_5CH_3(C)$

A is Acetylene, B is Benzene and C is Toluene.

4. Write the corresponding equations for the following reactions and name the products A, B, and C. $Ethylene \xrightarrow[CCl_4]{Br_2} (A) \xrightarrow{alc.KOH} (B) \xrightarrow{Br_2} (C)$

Ans. $C_2H_4 + Br_2 \xrightarrow[CCl_4]{} BrH_2C - CH_2Br + 2KOH \xrightarrow{-2KBr,-2H_2O} HC \equiv CH \xrightarrow{2Br_2} Br_2H\ C - CHBr_2$ A is 1,2-dibromo ethane , B is acetylene and C is1,1,2,2-tetrabromo ethane.

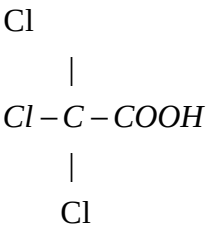
5. How do you prepare ethychloride from ethylene?

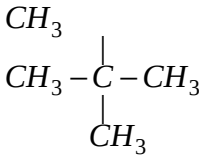
Ans. Ethychloride is prepared by the electrophilic addition of HCl to ethylene in presence of $AlCl_3$.

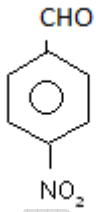
$$H_2C=CH_2+HCl \xrightarrow{AlCl_3} H_3C-CH_2Cl$$

6. Write structures of Trichloro ethanoic acid, Neopentane , P-nitro benzaldehyde?

Ans. Trichloro ethanoic acid Neopentane P-nitro benzaldehyde.



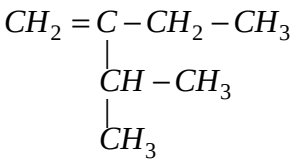




7. Write the IUPAC names of the following hydrocarbons:

(a) $CHC–CH_2–CH=CH–CH_3$

(b)



Ans. (a) Hex-4-en-1-yne

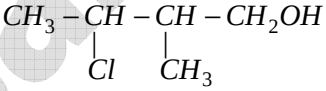
(b) 2-Ethyl-3-methyl-1-butene

8. Give the IUPAC names of the compounds:

i) $CH_3-C\equiv C-CH_3$

ii) $CH_3-CH_2-CH=CH_2$

iii)



Ans. i. 2-butyne

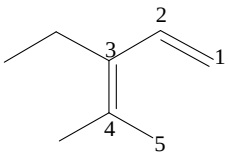
ii. 1-butene

iii. 3-chloro, 2-methyl1-butanol

9. Write the structural formula of the following:

(a) 3–Ethyl–4–methylpenta–1,3–diene

(b) 2-Methyl-3-hexyne

Ans. a. 

b . $CH_3CH_2C \equiv CCHCH_3$ with CH_3 branch

10. What is the stability order of various alkyl free radicals? Why?

Ans. The stability order of alkyl free radicals is:

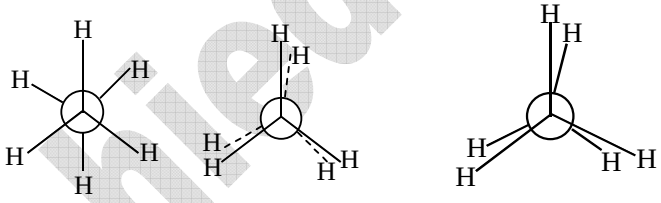
$(CH_3)_3\dot{C} > (CH_3)_2\dot{C}H > CH_3\dot{C}H_2 > \dot{C}H_3$

3^0 2^0 1^0

More the number of hyperconjugative structures, the greater is the stability. Tertiary butyl free radical has 9; isopropyl free radical has 6; ethyl free radical has 3 and methyl free radical has no hyperconjugative structures.

11. Write the conformations of Ethane?

Ans.



12. What is chain isomerism? Give Example?

Ans.

The isomerism arises due to difference in the arrangement of carbon atoms constituting the chain known as Chain isomerism

E.g. 1) Butane has two chain isomers.

$CH_3 - CH_2 - CH_2 - CH_3$ **and** $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

n-Butane Isobutane

13. What is metamerism? Give Example?

Ans.

The isomerism arises due to the presence of different alky l groups attached to the same bivalent functional group is called. Metamerism Ethers, secondary amines, ketones, etc., can exhibit metamerism.

1) $C_2H_5OC_2H_5$ **and** $C_3H_7OCH_3$

Diethylether Methyl propyl ether

2) $C_3H_7NHC_3H_7$ **and** $C_2H_5NHC_4H_9$

Dipropyl amine Ethyl butyl amine